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Zombie states for description of structure and dynamics of multi-electron systems

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Canonical Coherent States (CSs) of Harmonic Oscillator have been extensively used as a basis in a number of computational methods of quantum dynamics. However, generalising such techniques for fermionic systems is difficult because Fermionic Coherent States (FCSs) require complicated algebra of Grassmann numbers not well suited for numerical calculations. This paper introduces a coherent antisymmetrised superposition of "dead" and "alive" electronic states called here Zombie State (ZS), which can be used in a manner of FCSs but without Grassmann algebra. Instead, for Zombie States, a very simple sign-changing rule is used in the definition of creation and annihilation operators. Then, calculation of electronic structure Hamiltonian matrix elements between two ZSs becomes very simple and a straightforward technique for time propagation of fermionic wave functions can be developed. By analogy with the existing methods based on Canonical Coherent States of Harmonic Oscillator, fermionic wave functions can be propagated using a set of randomly selected Zombie States as a basis. As a proof of principles, the proposed Coupled Zombie States approach is tested on a simple example showing that the technique is exact. https://doi.org/10.1063/1.5023209

I. INTRODUCTION

In this short paper, a mathematical treatment of second quantization for fermions is proposed, which will be based on the introduction of a simpleminded, Coherent State (CS)-like object called here Zombie State (ZS). Fermionic Coherent States (FCSs)[1] are introduced as $|\eta_m\rangle = a(|0_m\rangle + \eta_m|1_m\rangle)$, where $|1_m\rangle$ and $|0_m\rangle$ are the m-th orbital and its vacuum state, respectively; a is a normalization factor; and η_m is not a number but an element of the Grassmann algebra. Grassmann algebra is needed to ensure correct permutational antisymmetry of multi-electron Fermionic Coherent States $|\boldsymbol{\eta}\rangle = a\prod_m(|0_m\rangle + \eta_m|1_m\rangle)$ and anticommutation of creation and annihilation operators, but Grassmann algebra is not convenient for numerical calculations. Complicated Wick's theorem should be used to evaluate the matrix elements between Fermionic CSs.[2]

This paper shows that a much simpler approach can be developed. We will define Zombie State (ZS) as Slater determinant of superpositions of "dead" and "alive" electrons, ensuring proper ZS permutational antisymmetry. Then, creation and annihilation operators will be defined with the help of a simple sign-changing rule. This rule can be trivially implemented in a computer code and matrix elements of second quantised Hamiltonian can easily be computed without Wick's theorem, normally used for standard FCSs.[2] After that, it will be shown that a basis of randomly selected set of Zombie States serves as a basis for quantum propagation similar to the existing Canonical Coherent States-based methods, such as Coupled Coherent States (CCS)[3] and variational Multiconfigurational Gaussians (vMCG),[4] for example. By analogy with CCS and vMCG, a new class of methods of quantum dynamics of Fermions can potentially be developed with Zombie States.

II. THEORY

Everywhere in this note, the term Zombie State (ZS) will refer to a superposition of "dead" or "alive" states $|1_m\rangle$ and $|0_m\rangle$

$$|\zeta_m(a_{1m}, a_{2m})\rangle = a_{1m}|1_m\rangle + a_{0m}|0_m\rangle = \begin{bmatrix} a_{1m} \\ a_{0m} \end{bmatrix}, \qquad (1)$$

which describe an occupied or unoccupied spin-orbital m. Zombie State (1) is similar to the SU(2) coherent states of a two-level system.[5] In SU(2) states, one of the coefficient is usually assumed to be real number and the other one is complex, but it does not have to be. Both a_{0m} and a_{1m} in the ZS (1) can be complex numbers, which would introduce an insignificant phase factor.

For a multi-electronic system, we assume that there are M simultaneously "dead" and "alive" Zombie electrons, one at each of the M spin-orbitals. Let us write M-particle ZS as a normalised Slater determinant made of M one electron Zombie States ζ_m:

$$|\boldsymbol{\zeta}\rangle = |\zeta_1, \zeta_2, \ldots, \zeta_M\rangle = \frac{1}{\sqrt{M!}} \det \begin{vmatrix} \zeta_1(1) & \zeta_2(1) & \ldots & \zeta_M(1) \\ \zeta_1(2) & \zeta_2(2) & \ldots & \zeta_M(2) \\ \ldots & \ldots & \ldots & \ldots \\ \zeta_1(M) & \zeta_2(M) & \ldots & \zeta_M(M) \end{vmatrix}. \qquad (2)$$

Notice that the $M \times M$ matrix in (2) is of the size of the number of orbitals. It is bigger than the $N \times N$ matrix of the size of the number of electrons, used in standard theories of electronic

structure.[6] A particular ZS Slater determinant $|\zeta^{(b)}\rangle$ given by Eq. (2) includes 2M amplitudes and can be denoted as

$$\left|\zeta^{(b)}\right\rangle = \begin{bmatrix} a_{11}^{(b)} & a_{12}^{(b)} & \dots & a_{1M}^{(b)} \\ a_{01}^{(b)} & a_{02}^{(b)} & \dots & a_{0M}^{(b)} \end{bmatrix}. \tag{3}$$

The first low index in the complex amplitude $a_{1m}^{(b)}$ or $a_{0m}^{(b)}$ is either 1 or 0 and labels "life" or "death," the index m is that of a spin-orbital, and the upper index (b) refers to particular ZS. Once the array of the amplitudes (3) is set, one can express various physical quantities via the amplitudes in the array, taking into account that it represents Slater determinant (2). For example, we can assume that all orbitals (dead and alive) are orthonormal, i.e.,

$$\langle 1_m|\, 1_n\rangle = \delta_{mn}, \quad \langle 0_m|\, 0_n\rangle = \delta_{mn}, \quad \langle 1_m|\, 0_n\rangle = 0. \tag{4}$$

Then, the overlap of two ZSs is given as

$$\Omega_{ab} = \left\langle \zeta^{(a)} \middle| \zeta^{(b)} \right\rangle = \prod_{m=1,M} \left(a_{1m}^{(a)\,*} a_{1m}^{(b)} + a_{0m}^{(a)\,*} a_{0m}^{(b)} \right). \tag{5}$$

Another example is the expression for the matrix elements of the Hamiltonian, which will be derived below.

A standard Fock Space "physical" electronic structure configuration with N electrons occupying N out of M orbitals are given by ZSs with N ones and M-N zeros in the 1st row, meaning N fully alive electrons (or N-occupied spin-orbitals) and M-N fully dead electrons (or unoccupied spin-orbitals),

$$\left|\zeta^{(110\dots1)}\right\rangle = \begin{bmatrix} 1 & 1 & 0 & \dots & 1 \\ 0 & 0 & 1 & \dots & 0 \end{bmatrix}. \tag{6}$$

Enumerating the Fock space configurations as a sequence of 1 and 0 is not new. For example, it has been used in Ref. 7 where it was shown to have certain bookkeeping advantages. The space of all 2^M Fock states ranging from zero occupancy $|\zeta^{(000\dots0)}\rangle$ to full occupancy $|\zeta^{(111\dots1)}\rangle$ will be refereed here as Full Fock Space (FFS). In this paper, we go further assuming arbitrary amplitudes of $|1_m\rangle$ and $|0_m\rangle$ in (1) and (3).

To find the matrix elements $\left\langle \zeta^{(a)} \middle| \hat{H} \middle| \zeta^{(b)} \right\rangle$ of the second quantized electronic structure Hamiltonian[6]

$$\hat{H} = \hat{H}_{norm} = \sum_{m,n} h_{mn} \hat{b}_m^+ \hat{b}_n + \frac{1}{2} \sum_{klmn} \hat{b}_k^+ \hat{b}_l^+ W_{klnm} \hat{b}_m \hat{b}_n \tag{7}$$

between two ZSs, one has to define the action of Fermionic creation and annihilation operators on the ZSs. In a customary fashion, the operators $\hat{b}$ and $\hat{b}^+$ act on a single orbital by creating and annihilating "dead" and "alive" states

$$\begin{aligned} &\hat{b}|1\rangle = |0\rangle, \quad \hat{b}|0\rangle = 0|1\rangle, \\ &\hat{b}^+|0\rangle = |1\rangle, \quad \hat{b}^+|1\rangle = 0|0\rangle, \end{aligned} \tag{8}$$

so that

$$\begin{aligned} &\hat{b}|\zeta\rangle = \hat{b}(a_1|1\rangle + a_0|0\rangle) = 0|1\rangle + a_1|0\rangle, \\ &\hat{b}^+|\zeta\rangle = \hat{b}^+(a_1|1\rangle + a_0|0\rangle) = a_0|1\rangle + 0|0\rangle \end{aligned} \tag{9}$$

or using the notations (1)

$$\begin{aligned} &\hat{b}|\zeta\rangle = \hat{b}\begin{bmatrix} a_1 \\ a_0 \end{bmatrix} = \begin{bmatrix} 0 \\ a_1 \end{bmatrix}, \\ &\hat{b}^+|\zeta\rangle = \hat{b}^+\begin{bmatrix} a_1 \\ a_0 \end{bmatrix} = \begin{bmatrix} a_0 \\ 0 \end{bmatrix}. \end{aligned} \tag{10}$$

For multi-electronic ZS, additional rule has to be introduced to ensure proper anti-commutation of the operators. The operators $\hat{b}_m^+$ and $\hat{b}_m$ act on the ZS (3) in the following way:

$$\begin{aligned} \hat{b}_m^+ \left|\zeta^{(b)}\right\rangle &= \begin{bmatrix} -a_{11}^{(b)} & -a_{12}^{(b)} & \dots & -a_{1m-1}^{(b)} & a_{0m}^{(b)} & a_{1m+1}^{(b)} & \dots & a_{1M}^{(b)} \\ a_{01}^{(b)} & a_{02}^{(b)} & \dots & a_{0m-1}^{(b)} & 0 & a_{0m+1}^{(b)} & \dots & a_{0M}^{(b)} \end{bmatrix}, \\ \hat{b}_m \left|\zeta^{(b)}\right\rangle &= \begin{bmatrix} -a_{11}^{(b)} & -a_{12}^{(b)} & \dots & -a_{1m-1}^{(b)} & 0 & a_{1m+1}^{(b)} & \dots & a_{1M}^{(b)} \\ a_{01}^{(b)} & a_{02}^{(b)} & \dots & a_{0m-1}^{(b)} & a_{1m}^{(b)} & a_{0m+1}^{(b)} & \dots & a_{0M}^{(b)} \end{bmatrix}. \end{aligned} \tag{11}$$

They not only act on the m-th column of the Slater determinant similar to the single electron case (8)–(10) but also change the sign of the "alive" states amplitudes $a_{1k}^{(b)}$ for all $k < m$ while leaving the amplitudes $a_{0k}^{(b)}$ of "dead" states unchanged. It is easy to verify that this additional sign-changing rule ensures the proper anticommutation of the operators, such as $\hat{b}_m^+ \hat{b}_n^+ \left|\zeta^{(b)}\right\rangle = -\hat{b}_n^+ \hat{b}_m^+ \left|\zeta^{(b)}\right\rangle$, etc. Indeed, if, for example, $m < n$, then

$$\begin{aligned} \hat{b}_m^+ \hat{b}_n^+ \left|\zeta^{(b)}\right\rangle &= \begin{bmatrix} a_{11}^{(b)} & a_{12}^{(b)} & \dots & a_{1m-1}^{(b)} & a_{0m}^{(b)} & -a_{1m+1}^{(b)} & \dots & -a_{n-1}^{(b)} & a_{0n}^{(b)} & a_{1n+1}^{(b)} & \dots & a_{1M}^{(b)} \\ a_{01}^{(b)} & a_{02}^{(b)} & \dots & a_{0m-1}^{(b)} & 0 & a_{0m+1}^{(b)} & \dots & a_{0n-1}^{(b)} & 0 & a_{0n+1}^{(b)} & \dots & a_{0M}^{(b)} \end{bmatrix}, \\ \hat{b}_n^+ \hat{b}_m^+ \left|\zeta^{(b)}\right\rangle &= \begin{bmatrix} a_{11}^{(b)} & a_{12}^{(b)} & \dots & a_{1m-1}^{(b)} & -a_{0m}^{(b)} & -a_{1m+1}^{(b)} & \dots & -a_{n-1}^{(b)} & a_{0n}^{(b)} & a_{1n+1}^{(b)} & \dots & a_{1M}^{(b)} \\ a_{01}^{(b)} & a_{02}^{(b)} & \dots & a_{0m-1}^{(b)} & 0 & a_{0m+1}^{(b)} & \dots & a_{0n-1}^{(b)} & 0 & a_{0n+1}^{(b)} & \dots & a_{0M}^{(b)} \end{bmatrix}. \end{aligned} \tag{12}$$

Both pairs of operators act on the columns m and n and also change the sign of $a_{1k}^{(b)}$ for $n < k < m$. In addition, in the latter pair $\hat{b}_n^+\hat{b}_m^+$, the operator $\hat{b}_n^+$ changes the sign of $a_{0m}^{(b)}$, which has previously been moved up to the first row by $\hat{b}_m^+$. Thus, the two Slater determinants (12) differ only by the sign of the m-th column. In a similar fashion, all other anticommutational rules for creation and annihilation operators can be verified. Simple observation (12) and the fact that $\hat{b}_m^+\hat{b}_m^+ = \hat{b}_m\hat{b}_m = 0$, which follows from (10), ensure that the definition (11) is correct. In Appendix A, the sign-changing rule (12) of the operators (11) is derived, starting from standard definition of creation and annihilation operators.[6,7] Here, we will only mention that the sign-changing rule in (11) originates from the fact that in the usual second quantization approach,[6] operating within the manifold of N-electron Slater determinants with no unoccupied spin-orbitals included, creation and annihilation operators act on the first column of the Slater determinant. As a result, when acting with $\hat{b}_m^+$ or $\hat{b}_m$, the m-th column must be moved to or from the first position, which is also equivalent to changing sign of all other occupied spin-orbitals on the left from m.

The operators (11) are easy to implement in a computer code. Then the matrix elements of the operator (7) can be calculated as follows:

$$H_{ab} = \left\langle \zeta^{(a)} \middle| \hat{H} \middle| \zeta^{(b)} \right\rangle = \sum_{m,n} h_{m,n} \left\langle \zeta^{(a)} \middle| \zeta_{mn}^{(b)} \right\rangle + \frac{1}{2} \sum_{m,n} W_{klnm} \left\langle \zeta^{(a)} \middle| \zeta_{klmn}^{(b)} \right\rangle, \quad (13)$$

where $\left|\zeta_{klmn}^{(b)}\right\rangle = \hat{b}_k^+\hat{b}_l^+\hat{b}_m\hat{b}_n\left|\zeta^{(b)}\right\rangle$ and $\left|\zeta_{mn}^{(b)}\right\rangle = \hat{b}_m^+\hat{b}_n\left|\zeta^{(b)}\right\rangle$ are generated by sequentially applying (11), and their overlaps $\left\langle \zeta^{(a)} \middle| \zeta_{mn}^{(b)} \right\rangle$ and $\left\langle \zeta^{(a)} \middle| \zeta_{klmn}^{(b)} \right\rangle$ with $\langle\zeta^{(a)}|$ are given by (5).

Thus, introduction of Zombie States, which can be viewed as antisymmetrised Coherent States of a set of two-level systems, and the form of second quantization electronic structure Hamiltonian given by (11) and (13) on the manifold of Zombie States (2) is the first result of this paper. In Sec. III, it is shown how a basis of ZSs can be used for quantum propagation in a manner similar to the CCS technique that employs Canonical Coherent States of Harmonic Oscillator for quantum dynamics of distinguishable particles.

III. WORKING EQUATIONS

Unlike standard FCSs, ZSs do not require Grassmann algebra and calculation of the matrix elements between them is straightforward. The new form of second quantization described above can be used for practical numerical calculations.

Previously it was demonstrated that a relatively small basis of randomly selected, trajectory-guided Canonical Coherent States of HO can accurately represent quantum dynamics of a system with many distinguishable particles and many degrees of freedom. A tempting opportunity is to use ZSs for electron dynamics in a similar fashion. One can generate a basis of K ZSs so that the identity operator will be given as

$$\hat{\mathbf{I}} = \sum_{a,b=1,K} \left|\zeta^{(b)}\right\rangle \Omega_{ba}^{-1} \left\langle \zeta^{(a)} \right|. \quad (14)$$

Any physical N-electron wave function $|\Psi\rangle$, which is a superposition of a set of N-electron Fock configurations (9), can be projected on the basis of K Zombie States and written as their superposition

$$|\Psi\rangle = \hat{\mathbf{I}}|\Psi\rangle = \sum_{a,b=1,K} \left|\zeta^{(b)}\right\rangle \Omega_{ba}^{-1} \left\langle \zeta^{(a)} \middle| \Psi \right\rangle = \sum_{b=1,K} A^{(b)} \left|\zeta^{(b)}\right\rangle. \quad (15)$$

Each of the basis ZSs $|\zeta^{(b)}\rangle$ contains contributions from all N-electron Fock Space configurations. Also, each $|\zeta^{(b)}\rangle$ contains nonphysical contributions with the number of electrons smaller or larger than N, but in the superposition (15) they effectively cancel each other out. This feature is similar to that of the Hartree-Fock-Bogoliubov (HFB) approach, where the states with all possible occupancies are involved, but the "unphysical" occupancies compensate each other[8] even in a single determinant. Recently, HFB has been used in electronic structure theory for constructing new density functional.[9] The hope now is that with some good sampling of the ZS basis $|\zeta^{(b)}\rangle$, the number of ZSs in the expansion (15) with a small number of ZSs will be sufficient for accurate description of electronic structure and dynamics, just like a small number of Canonical Coherent States can describe the dynamics of complicated quantum systems of distinguishable particles (for instance coupled molecular vibrations) within the Coupled Coherent States (CCS) method[3] where a superposition of multidimensional Gaussian Coherent States,

$$|\Psi\rangle = \sum_{b=1,k} A^{(b)} \left|\mathbf{z}^{(b)}\right\rangle \quad (16)$$

is used as the ansatz for the wave function. Each multidimensional many-body coherent state

$$\left|\mathbf{z}^{(b)}\right\rangle = \left|z_1^{(b)}\right\rangle ... \left|z_M^{(b)}\right\rangle. \quad (17)$$

is a product of 1D CS and similarly to (3) coherent state (17) can be labeled by the array of complex numbers $|\mathbf{z}^{(b)}\rangle = [z_1^{(b)}, \ldots, z_M^{(b)}]$. A 1D Canonical CS is a Gaussian wave packet $\langle x|z\rangle = \langle x|q,p\rangle = \sqrt{\frac{\gamma}{2}} \exp\left(-\frac{\gamma}{2}(x-q)^2 + ip(x-q) + i\frac{qp}{2}\right)$, where $z = \frac{\gamma^{1/2}q + p(\gamma^{1/2}\hbar)^{-1}}{2^{1/2}}$ and $\gamma^{-1/2}$ is the width of the wave packet localised near the phase space point q,p. Several Canonical Gaussian Coherent States-based methods have been developed and proved to be valuable techniques of atomistic simulations. They have been used extensively to model the dynamics of nuclei in molecules for chemical reaction dynamics,[10,11] in simulations of the dynamics of electrons in strong laser field,[12] in simulations of quantum decoherence,[13] etc. An important feature of the Canonical CS-based methods, which makes them particularly efficient, is that the basis CSs is time-dependent. The evolution of the wave function in the Coupled Coherent States technique is described by the trajectories $|\mathbf{z}^{(b)}(t)\rangle$ and time dependence of their amplitudes $A^{(b)}(t)$. These ideas developed for Canonical Coherent States previously can now be generalised for fermionic ZSs.

In the Coupled Zombie States (CZS) method, we will describe the time evolution of wave function by that of ZSs amplitudes $A^{(b)}(t)$ and "trajectories" $|\zeta^{(b)}(t)\rangle$ in Eq. (15). If the basis set of ZSs $|\zeta^{(b)}(t)\rangle$ is time-dependent, the Schrödinger equation for the wave function (15) becomes a system of linear equations for $\frac{dA^{(b)}}{dt}$

$$\sum_{b=1,K}\left\langle\zeta^{(a)}\middle|\zeta^{(b)}\right\rangle\frac{dA^{(b)}}{dt} = -\sum_{b=1,K}\left\langle\zeta^{(a)}\middle|\frac{d\zeta^{(b)}}{dt}\right\rangle A^{(b)} - i\sum_{b=1,K}\left\langle\zeta^{(a)}\middle|\hat{H}\middle|\zeta^{(b)}\right\rangle A^{(b)}. \quad (18)$$

Following the Coupled Coherent States methods[3,10] for Canonical Coherent States in the Coupled Zombie States approach, the analogue of classical Hamilton's equation

$$\frac{d\zeta^{(b)}}{dt} = -i\frac{\partial\left\langle\zeta^{(b)}\middle|\hat{H}\middle|\zeta^{(b)}\right\rangle}{\partial\zeta^{(b)\,*}} \quad (19)$$

can be used to find the trajectory of ZSs $|\zeta^{(b)}(t)\rangle$. Similarly to the CCS method, in the CZS, Eq. (19) for the trajectory can be derived from variational principle applied to the ZS $|\zeta^{(b)}\rangle$. See Appendix B for variational approach to the ZS dynamics.

Calculating the derivatives in (19) can be done in a very efficient way, which does not even require a separate subroutine. Instead, the algorithm for the matrix element (13) described above can be used. See Appendix C.

Unlike single configuration methods like time-dependent Hartree-Fock-Bogoliubov (TDHFB),[2] for example, the proposed Coupled Zombie States approach is based on the multiconfigurational wave function (15). CZS uses not a single "trajectory" of a single Slater Determinant but a set of them (19) together with the coupled equation (18) for the amplitudes of trajectory-guided ZSs. This makes CZS equations (18) and (19) formally exact in a sense that it can in principle be converged to the exact result.

Equations (18) and (19) are the second result of this paper. They represent the simplest way of fermionic wave function propagation based on time-dependent Zombie States and were written by analogy with the equations of the Couple Coherent States,[3] which exploits Coherent States of Harmonic Oscillator. Similarly to CCS, in CZS, we assume that time dependence of basis set functions is predetermined by Eq. (19).

IV. PROOF OF PRINCIPLES WITH NUMERICAL EXAMPLES

As a proof of principle, the CZS equations (18) and (19) were applied to the LiH system with $N = 4$ electrons on 3 spatial orbitals (M = 6 spin-orbitals). The Hartree-Fock orbitals and the integrals h_{nm} and W_{klnm} were produced by the MOLPRO program[14] with 6-31G** basis. The basis of $K = 2^6$ ZSs with randomly selected amplitudes a_{1m} or a_{0m} was generated. Although random, such basis is complete in the Full Fock Space. The overlap matrix Ω_{ab} (5) and the Hamiltonian matrix H_{ab} (12) were calculated for the basis of nonorthogonal ZSs and the eigen values were found. All 64 eigen values, corresponding to the number of electrons N ranging from 0 to 6 were exact and indistinguishable from those given by the MOLPRO Full Configuration Interaction (Full CI) approach[6] and also by diagonalization of the matrix elements of the Hamiltonian (12) in the Full Fock Space basis (6).

Similarly, for the Li_2 with 6 electrons and 10 spin-orbitals, the integrals h_{nm} and W_{klnm} were produced, also with 6-31G** basis. Then the basis of $K = 2^{10}$ Zombie States was generated and 2^{10} eigen values of the electronic structure Hamiltonian (7) were calculated with high precision for all possible numbers of electrons ranging from 0 to 10. They also were in perfect agreement with those obtained by MOLPRO Full CI and by diagonalization of the Hamiltonian (13) in the basis (6). Therefore, using simple sign-changing rule (11) in the definition of creation and annihilation operators is exact and ZSs with the sign-changing rule (11) can be used as a basis set for numerical calculations instead of Fock Space functions (6) or Fermionic CSs with Grassmann algebras.[1]

After finding eigen values E_n and eigen vectors $|\phi_n\rangle$ in Full Fock Space electronic propagator written as

$$e^{-i\hat{H}t} = \sum_n |\phi_n\rangle e^{-iE_nt}\langle\phi_n| \quad (20)$$

provides the benchmark with which propagation with the CZS equations (18) and (19) can be compared. One of the LiH molecule Hartree-Fock configurations was selected as initial condition. It was expanded on the basis of 64 random ZSs and propagated using Eqs. (18) and (19), which yields the time-dependent wave function (15) $|\Psi(t)\rangle = \sum_{b=1,K} A^{(b)}(t)\left|\zeta^{(b)}(t)\right\rangle$. Figure 1(a) shows the absolute value of rapidly oscillating autocorrelation function $\langle\Psi(0)|\Psi(t)\rangle = \sum_{b=1,K} A^{(b)}(t)\left\langle\Psi(0)\middle|\zeta^{(b)}(t)\right\rangle$. The CZS autocorrelation function is indistinguishable from that obtained with the benchmark propagator (20). Figure 1(b) shows Fourier transform of the autocorrelation function. Positions of the peaks seen at Fig. 1(b) correspond to the energies of the electronic states of the LiH molecule to which the selected Hartree-Fock configuration contributes most.

Given that high resolution spectrum shown in Fig. 1 requires very long time dynamics, time-dependent propagation is not an efficient way to extract eigen values of the electronic structure Hamiltonian. The purpose of the result shown in Fig. 1 is only to demonstrate that Eqs. (18) and (19) can produce exact time-dependent wave functions.

The CZS equations (18) and (19) are very similar to those used in the CCS method, with the difference that here Zombie States are used instead of Harmonic Oscillator CSs. In Ref. 15, it was shown that similar equations can be derived not only for Canonical Coherent States but for many other types of Coherent States as well. The current paper shows how this philosophy can be applied specifically to Zombie States. Other forms of the equations of motion for the ZS-based wave function (15) can be constructed by analogy with the Canonical Coherent States methods other than CCS. For example, full variational principle can be applied

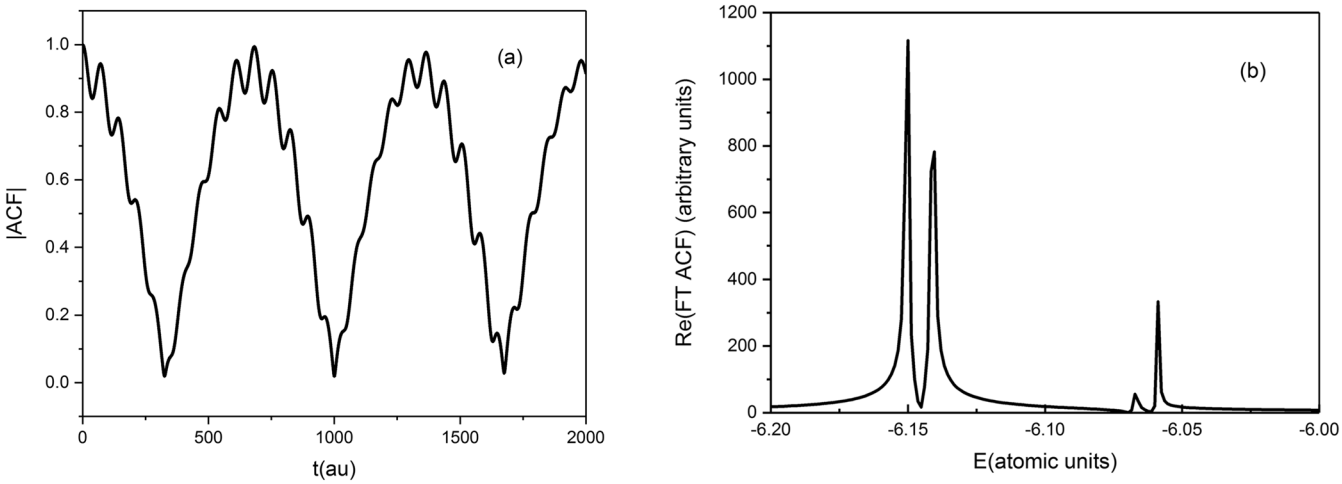

FIG. 1. Frame (a) shows the absolute value of rapidly oscillating autocorrelation function $\langle \mathbf{\Psi}(0)|\mathbf{\Psi}(t)\rangle$, calculated by propagating a single Hartree-Fock configuration on the basis of randomly selected Zombie States. Real part of the autocorrelation function Fourier transform is shown in the frame (b). The positions of the peaks correspond to the exact eigen values of electronic structure Hamiltonian.

to the wave function (15) to obtain Variational Multiconfigurational Zombie States (vMCZS) similar to the method of Variational Multiconfigurational Gaussians,[4,16] which uses more sophisticated variational trajectories.[17] See Appendix B, where vMCZS equations are derived by the analogy with vMCG.

Many methods to treat the dynamics of many-body fermionic systems are known in the literature. For example, several versions of Multiconfigurational Time-Dependent Hartree-Fock (MCTDH-F) techniques have been developed,[7,18–25] which can treat numerically many-body fermionic systems. Time-Dependent Restricted-Active-Space Self-Consistent Field (TD-RASSCF) theory[26–29] has been proposed to treat laser-driven many-electron dynamics at lower computational cost. Another example is B-spline Time-Dependent Algebraic Diagrammatic Construction (B-spline TD-ADC) approach[30] that has been used to calculate the spectra of High-Harmonic generation in many-electron systems.[31] In the past, Coherent States-based techniques[32] were able to treat quantum systems of distinguishable particles with many degrees of freedom,[33,34] in some cases providing simple alternative to MCTDH. Good sampling of Coherent State basis was always the key to efficiency of the CS-based methods. In the systems with larger number of electrons and orbitals, generating complete basis set, as has been done in the numerical examples above, will not be possible. Nevertheless, all sampling tricks previously developed for Canonical Coherent States of HO can be generalised for the Zombie States as well. The hope is that a small basis set of ZSs may work, but whether CZS will be sufficiently efficient and accurate remains to be seen.

One of the possible situations where Coupled Zombie States may have an advantage would be to use ZSs for direct dynamics simulations of nonadiabatic transitions in chemical dynamics. Currently, the methods based on Canonical Coherent States of HO are used to simulate the nuclear wave function in direct dynamics. Electrons are treated in adiabatic basis.[10,11] Calculating adiabatic potential energy surfaces and nonadiabatic coupling matrix elements (NACME) with the help of Electronic structure theory is the most computationally expensive part. Treating electronic part with Zombie States would require only cheap Hartree-Fock electronic structure. Also, both electronic and nuclear parts of the wave function would be treated on the same formal footing as a superposition of trajectory-guided combined Zombie States and Canonical Coherent States,

$$|\Psi\rangle = \sum_{b=1,K} A^{(b)} \left|\boldsymbol{\zeta}^{(b)}\right\rangle \left|\mathbf{z}^{(b)}\right\rangle. \tag{21}$$

In the future work, we shall see how far the CZS approach can be pushed for treatment of the dynamics of fermions. This will be possible only if nonphysical contributions to each individual Zombie State $|\boldsymbol{\zeta}^{(b)}\rangle$ cancel out in the sum (15). Whether this will be the case remains to be seen. This note only sets the stage for future development of new methods by defining convenient Zombie States and deriving the second quantization Hamiltonian (13) based on the creation and annihilation operators (11). As second quantization is a very popular technique, its new ZS-based form can be of rather broad interest.

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APPENDIX A: DERIVATION OF THE SIGN-CHANGING RULE

A Slater determinant (2) can be presented as a sum of two Slater determinants as follows:

$$\sqrt{M!}|\zeta\rangle = \begin{vmatrix} (a_{11}|1_1(1)\rangle + a_{01}|0_1(1)\rangle) & (a_{12}|1_2(1)\rangle + a_{02}|0_2(1)\rangle) & \dots & (a_{1M}|1_M(1)\rangle + a_{0M}|0_M(1)\rangle) \\ (a_{11}|1_1(2)\rangle + a_{01}|0_1(2)\rangle) & (a_{12}|1_2(2)\rangle + a_{02}|0_2(2)\rangle) & \dots & (a_{1M}|1_M(2)\rangle + a_{0M}|0_M(2)\rangle) \\ \dots & \dots & \dots & \dots \\ (a_{11}|1_1(M)\rangle + a_{01}|0_1(M)\rangle) & (a_{12}|1_2(M)\rangle + a_{02}|0_2(M)\rangle) & \dots & (a_{1M}|1_M(M)\rangle + a_{0M}|0_M(M)\rangle) \end{vmatrix}$$

$$= a_{11} \begin{vmatrix} (|1_1(1)\rangle + 0 \times |0_1(1)\rangle) & (a_{12}|1_2(1)\rangle + a_{02}|0_2(1)\rangle) & \dots & (a_{1M}|1_M(1)\rangle + a_{0M}|0_M(1)\rangle) \\ (|1_1(2)\rangle + 0 \times |0_1(2)\rangle) & (a_{12}|1_2(2)\rangle + a_{02}|0_2(2)\rangle) & \dots & (a_{1M}|1_M(2)\rangle + a_{0M}|0_M(2)\rangle) \\ \dots & \dots & \dots & \dots \\ (|1_1(M)\rangle + 0 \times |0_1(M)\rangle) & (a_{12}|1_2(M)\rangle + a_{02}|0_2(M)\rangle) & \dots & (a_{1M}|1_M(M)\rangle + a_{0M}|0_M(M)\rangle) \end{vmatrix}$$

$$+ a_{01} \begin{vmatrix} (0 \times |1_1(1)\rangle + |0_1(1)\rangle) & (a_{12}|1_2(1)\rangle + a_{02}|0_2(1)\rangle) & \dots & (a_{1M}|1_M(1)\rangle + a_{0M}|0_M(1)\rangle) \\ (0 \times |1_1(2)\rangle + |0_1(2)\rangle) & (a_{12}|1_2(2)\rangle + a_{02}|0_2(2)\rangle) & \dots & (a_{1M}|1_M(2)\rangle + a_{0M}|0_M(2)\rangle) \\ \dots & \dots & \dots & \dots \\ (0 \times |1_1(M)\rangle + |0_1(M)\rangle) & (a_{12}|1_2(M)\rangle + a_{02}|0_2(M)\rangle) & \dots & (a_{1M}|1_M(M)\rangle + a_{0M}|0_M(M)\rangle) \end{vmatrix}. \quad \text{(A1)}$$

Equation (A1) follows from the fact that Slater determinant with a sum $a_{11}|1_1(1)\rangle + a_{01}|0_1(1)\rangle$ in the first column can be represented as a sum of two Slater determinants that include $a_{11}|1_1(1)\rangle$ and $a_{01}|0_1(1)\rangle$ only. Also, a zero can be added so that $a_{11}|1_1(1)\rangle = a_{11}|1_1(1)\rangle + 0 \times |0_1(1)\rangle$ and $a_{01}|0_1(1)\rangle = 0 \times |1_1(1)\rangle + a_{01}|0_1(1)\rangle$ and the coefficients a_{01} and a_{11} can be written in front of the determinants. In shorter notations (3), (A1) becomes

$$\begin{bmatrix} a_{11} & a_{12} & \dots & a_{1M} \\ a_{01} & a_{02} & \dots & a_{0M} \end{bmatrix} = a_{11} \begin{bmatrix} 1 & a_{12} & \dots & a_{1M} \\ 0 & a_{02} & \dots & a_{0M} \end{bmatrix} + a_{01} \begin{bmatrix} 0 & a_{12} & \dots & a_{1M} \\ 1 & a_{02} & \dots & a_{0M} \end{bmatrix}. \quad \text{(A2)}$$

Then, each of the two Slater determinants on the right-hand side of (A2) can be expanded as a sum of two determinants again—this time with respect to the second column, so that

$$\begin{bmatrix} a_{11} & a_{12} & \dots & a_{1M} \\ a_{01} & a_{02} & \dots & a_{0M} \end{bmatrix} = a_{11}a_{12} \begin{bmatrix} 1 & 1 & \dots & a_{1M} \\ 0 & 0 & \dots & a_{0M} \end{bmatrix} + a_{11}a_{02} \begin{bmatrix} 1 & 0 & \dots & a_{1M} \\ 0 & 1 & \dots & a_{0M} \end{bmatrix}$$

$$+ a_{01}a_{12} \begin{bmatrix} 0 & 1 & \dots & a_{1M} \\ 1 & 0 & \dots & a_{0M} \end{bmatrix} + a_{01}a_{02} \begin{bmatrix} 0 & 0 & \dots & a_{1M} \\ 1 & 1 & \dots & a_{0M} \end{bmatrix}. \quad \text{(A3)}$$

Repeating this procedure M times, we get

$$\sqrt{M!}|\zeta\rangle = a_{11}a_{12}\dots a_{1M} \begin{bmatrix} 1 & 1 & \dots & 1 \\ 0 & 0 & \dots & 0 \end{bmatrix} + a_{01}a_{12}\dots a_{1M} \begin{bmatrix} 0 & 1 & \dots & 1 \\ 1 & 0 & \dots & 0 \end{bmatrix} + \dots + a_{01}a_{02}\dots a_{0M} \begin{bmatrix} 0 & 0 & \dots & 0 \\ 1 & 1 & \dots & 1 \end{bmatrix}$$

$$= \sqrt{M!}(a_{11}a_{12}\dots a_{1M}|\zeta_{11\dots1}\rangle + a_{11}a_{02}\dots a_{1M}|\zeta_{10\dots1}\rangle + \dots + a_{01}a_{02}\dots a_{0M}|\zeta_{00\dots0}\rangle), \quad \text{(A4)}$$

where the sum on the right-hand side of (A4) contains all possible Fock States expressed as Zombie States with all possible combinations of 1 and 0. The products in front of them contain the amplitudes of populated dead or alive states.

It is well known how operators $\hat{b}_m$ and $\hat{b}_m^+$ act on the Fock states (see, for example, Ref. 7). In addition to acting with the operator $\hat{b}_m$ or $\hat{b}_m^+$ on the m-th column of a Fock State Slater Determinant on the right-hand side of (A4), one has to add additional factor of

$$f = (-1)^{n(m)}, \quad \text{(A5)}$$

where $n(m)$ is the number of occupied orbitals (having 1 in the upper row) with $k < m$, which are on the left from the m-th column. The factor (A5) is needed to ensure the correspondence with the standard definition of creation and annihilation operators in second quantization.[6] Multiplying by the factor (A5) is equivalent to changing sign in all coefficients a_{1k} for $k < m$, which proves the sign-changing rule (11).

APPENDIX B: VARIATIONAL MULTICONFIGURATIONAL ZOMBIE STATES (vMCZS)

The equations for the time dependence of the parameters of the function

$$|\Psi(t)\rangle = \sum_{b=1,K} A^{(b)}(t)\left|\zeta^{(b)}(t)\right\rangle \tag{B1}$$

can be determined from variational principle in exactly the same way it was done previously for Canonical Coherent States.[16] Variational functional can be recognised as Lagrangian

$$L = \langle\Psi|\frac{i}{2}\left(\frac{\vec{\partial}}{\partial t} - \frac{\overleftarrow{\partial}}{\partial t}\right) - \hat{H}|\Psi\rangle, \tag{B2}$$

which depends on all parameters of the wave function $A^{(1)},\ldots, A^{(K)}$ $a_{01}^{(1)}\ldots a_{0M}^{(1)},\ldots, a_{01}^{(K)}\ldots a_{0M}^{(K)}$; their time derivatives $\dot{A}^{(1)},\ldots,\dot{A}^{(K)}$ $\dot{a}_{01}^{(1)}\ldots\dot{a}_{0M}^{(1)},\ldots,\dot{a}_{01}^{(K)}\ldots\dot{a}_{0M}^{(K)}$; and their complex conjugate. Simple differentiation yields

$$\begin{aligned}
L &= \sum_{a,b}\left\{\frac{i}{2}\left[\left\langle\zeta^{(a)}\middle|\dot{\zeta}^{(b)}\right\rangle - \left\langle\dot{\zeta}^{(a)}\middle|\zeta^{(b)}\right\rangle\right]A^{(a)\,*}A^{(b)} + \left[A^{(a)\,*}\dot{A}^{(b)} - \dot{A}^{(a)\,*}A^{(b)}\right]\left\langle\zeta^{(a)}\middle|\zeta^{(b)}\right\rangle - A^{(a)\,*}A^{(b)}\left\langle\zeta^{(a)}\middle|\hat{H}\middle|\zeta^{(b)}\right\rangle\right\} \\
&= \sum_{a,b}\frac{i}{2}\left\{A^{(a)\,*}A^{(b)}\sum_j\left[a_{1j}^{(a)\,*}\dot{a}_{1j}^{(b)} - \dot{a}_{1j}^{(a)\,*}a_{1j}^{(b)} + a_{0j}^{(a)\,*}\dot{a}_{0j}^{(b)} - \dot{a}_{0j}^{(a)\,*}a_{0j}^{(b)}\right]\prod_{k\neq j}\left(a_{1k}^{(a)\,*}a_{1k}^{(b)} + a_{0k}^{(a)\,*}a_{0k}^{(b)}\right)\right\} \\
&+ \sum_{a,b}\left\{\frac{i}{2}\left[A^{(a)\,*}\dot{A}^{(b)} - \dot{A}^{(a)\,*}A^{(b)}\right]\prod_k\left(a_{1k}^{(a)\,*}a_{1k}^{(b)} + a_{0k}^{(a)\,*}a_{0k}^{(b)}\right)\right\} \\
&- \sum_{a,b}\left\{A^{(a)\,*}A^{(b)}H\left(a_{11}^{(a)\,*}\ldots a_{1M}^{(a)\,*}, a_{01}^{(a)\,*}\ldots a_{0M}^{(a)\,*}, a_{11}^{(b)}\ldots a_{1M}^{(b)}, a_{01}^{(b)}\ldots a_{0M}^{(b)}\right)\right\}.
\end{aligned} \tag{B3}$$

The Hamiltonian matrix elements $H\left(a_{11}^{(a)\,*}\ldots a_{1M}^{(a)\,*}, a_{01}^{(a)\,*}\ldots a_{0M}^{(a)\,*}, a_{11}^{(b)}\ldots a_{1M}^{(b)}, a_{01}^{(b)}\ldots a_{0M}^{(b)}\right)$ are given by (13). Then the equations of motion are simply the Lagrange equations

$$\frac{\partial L}{\partial\boldsymbol{\alpha}} - \frac{d}{dt}\frac{\partial L}{\partial\dot{\boldsymbol{\alpha}}} = 0, \frac{\partial L}{\partial\boldsymbol{\alpha}^{\,*}} - \frac{d}{dt}\frac{\partial L}{\partial\dot{\boldsymbol{\alpha}}^{\,*}} = 0, \tag{B4}$$

where $\boldsymbol{\alpha} = \left(A^{(1)},\ldots,A^{(K)}, a_{11}^{(1)}\ldots a_{1M}^{(1)},\ldots,a_{11}^{(K)}\ldots a_{1M}^{(K)}, a_{01}^{(1)}\ldots a_{0M}^{(1)},\ldots,a_{01}^{(K)}\ldots a_{0M}^{(K)}\right)$ is the vector of wave function parameters. Similarly to Ref. 16, the Lagrange equations (B4) result in a system of simultaneous linear equations for the derivatives $\dot{\boldsymbol{\alpha}}$ of the wave function parameters.

If the wave function (B1) consists of only one ZS,

$$|\Psi(t)\rangle = A^{(b)}(t)\left|\zeta^{(b)}(t)\right\rangle \tag{B5}$$

variational principle yields trajectory (19). In the CZS (18), (19) approach, we do not use fully variational trajectories (B4) but much more simple trajectories (19) obtained from variational principle applied to single ZS. However, as the wave function (16) contains contributions from many basis ZSs, the coupled equations (18) for their amplitudes make CZS formally exact. The relationship between CZS and vMCZS approaches is exactly the same as between CCS[3] and vMCG[4] as described in Refs. 16 and 33.

APPENDIX C: DERIVATIVES OF THE ELECTRONIC STRUCTURE HAMILTONIAN

Partial derivatives in Equations (19) and (B4) can be calculated with a very efficient trick. Notice that the Hamiltonian matrix elements (13) include the overlaps $\left\langle\zeta^{(a)}\middle|\zeta^{(b)\prime}\right\rangle = \prod_{m=1,M}\left(a_{1m}^{(a)\,*}a_{1m}^{(b)\prime} + a_{0m}^{(a)\,*}a_{0m}{}^{(b)\prime}\right)$, where $\left|\zeta^{(b)\prime}\right\rangle$ is either $\left|\zeta_{klmn}^{(b)}\right\rangle = \hat{b}_k^+\hat{b}_l^+\hat{b}_m\hat{b}_n\left|\zeta^{(b)}\right\rangle$ or $\left|\zeta_{mn}^{(b)}\right\rangle = \hat{b}_m^+\hat{b}_n\left|\zeta^{(b)}\right\rangle$. Differentiating the overlap with respect to say $a_{1m}^{(a)\,*}$ yields

$$\begin{aligned}
\frac{\partial\left\langle\zeta^{(a)}\middle|\zeta^{(b)\prime}\right\rangle}{\partial a_{1m}^{(a)\,*}} &= a_{1k}^{(b)\prime}\prod_{m\neq k}\left(a_{1m}^{(a)\,*}a_{1m}^{(b)\prime} + a_{0m}^{(a)\,*}a_{0m}^{(b)\prime}\right) \\
&= \left(1\times a_{1k}^{(b)\prime} + 0\times a_{0k}^{(b)\prime}\right) \\
&\times\prod_{m\neq k}\left(a_{1m}^{(a)\,*}a_{1m}^{(b)\prime} + a_{0m}^{(a)\,*}a_{0m}^{(b)\prime}\right) \\
&= \left\langle\zeta^{(a)\prime\prime}\middle|\,\zeta^{(b)\prime}\right\rangle,
\end{aligned} \tag{C1}$$

which is the overlap of $|\zeta^{(b)\prime}\rangle$ with another ZS $\langle\zeta^{(a)\prime\prime}|$ obtained from $\langle\zeta^{(a)}|$ by replacing $a_{1k}^{(a)\,*}$ with 1 and $a_{0k}^{(a)\,*}$ with 0. Therefore,

$$\frac{\partial\left\langle\zeta^{(b)}\middle|\hat{H}\middle|\zeta^{(b)}\right\rangle}{\partial a_{1k}^{(b)\,*}} = \left\langle\zeta^{(b)\prime\prime}\middle|\hat{H}\middle|\zeta^{(b)}\right\rangle. \tag{C2}$$

Differentiating with respect to $a_{0m}^{(a)\,*}$ is done in a similar way but by replacing $a_{1k}^{(a)\,*}$ with 0 and $a_{0k}^{(a)\,*}$ with 1. Thus, calculating derivatives of the Hamiltonian in (19) and (B4) does not even require a separate subroutine and can be done simply with the algorithm for the matrix element (13) described above.

[1] J. Klauder and B. Skagerstam, *Coherent States Applications in Physics and Mathematical Physics* (World Scientific, New Jersey, 1985).
[2] J. P. Blaizot and G. Ripka, *Quantum Theory of Finite Systems* (MIT Press, Cambridge, MA, 1986).
[3] D. V. Shalashilin and M. S. Child, Chem. Phys. **304**, 103 (2004).
[4] G. A. Worth and I. Burghardt, Chem. Phys. Lett. **368**, 502 (2003).
[5] A. Perelomov, *Generalized Coherent States and Their Applications* (Springer Berlin Heidelberg, 2012).

[6]A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Dover Publications, 1989).
[7]A. I. Streltsov, O. E. Alon, and L. S. Cederbaum, Phys. Rev. A **81**(12), 022124 (2010).
[8]N. N. Bogolyubov, Soviet Phys.-Usp. **2**, 236 (1959).
[9]V. N. Staroverov and G. E. Scuseria, J. Chem. Phys. **117**, 11107 (2002).
[10]M. Ben-Nun and T. J. Martínez, *Advances in Chemical Physics* (John Wiley & Sons, Inc., 2002), p. 439.
[11]D. V. Makhov, C. Symonds, S. Fernandez-Alberti, and D. V. Shalashilin, Chem. Phys. **493**, 200 (2017).
[12]A. Kirrander and D. V. Shalashilin, Phys. Rev. A **84**, 033406 (2011).
[13]S. Y. Ye, D. Shalashilin, and A. Serafini, Phys. Rev. A **86**(12), 032312 (2012).
[14]H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **2**, 242 (2012).
[15]A. Grigolo, T. F. Viscondi, and M. A. M. de Aguiar, J. Chem. Phys. **144**(15), 094106 (2016).
[16]D. V. Shalashilin and I. Burghardt, J. Chem. Phys. **129**(9), 084104 (2008).
[17]P. Kramer and M. Saraceno, *Geometry of the Time-Dependent Variational Principle in Quantum Mechanics* (Springer Berlin Heidelberg, 2014).
[18]M. Nest, Chem. Phys. Lett. **472**, 171 (2009).
[19]M. Nest, T. Klamroth, and P. Saalfrank, Z. Phys. Chem. **224**, 569 (2010).
[20]I. S. Ulusoy and M. Nest, J. Chem. Phys. **136**(5), 054112 (2012).
[21]J. Caillat, J. Zanghellini, M. Kitzler, O. Koch, W. Kreuzer, and A. Scrinzi, Phys. Rev. A **71**(13), 012712 (2005).
[22]O. Koch, W. Kreuzer, and A. Scrinzi, Appl. Math. Comput. **173**, 960 (2006).
[23]O. E. Alon, A. I. Streltsov, and L. S. Cederbaum, Phys. Rev. A **76**(10), 062501 (2007).
[24]O. E. Alon, A. I. Streltsov, and L. S. Cederbaum, J. Chem. Phys. **127**(6), 154103 (2007).
[25]O. E. Alon, A. I. Streltsov, K. Sakmann, A. U. J. Lode, J. Grond, and L. S. Cederbaum, Chem. Phys. **401**, 2 (2012).
[26]H. Miyagi and L. B. Madsen, Phys. Rev. A **87**(12), 062511 (2013).
[27]H. Miyagi and L. B. Madsen, Phys. Rev. A **89**(15), 063416 (2014).
[28]H. Miyagi and L. B. Madsen, J. Chem. Phys. **140**(6), 164309 (2014).
[29]H. Miyagi and L. B. Madsen, Phys. Rev. A **95**(19), 023415 (2017).
[30]M. Ruberti, V. Averbukh, and P. Decleva, J. Chem. Phys. **141**(16), 164126 (2014).
[31]M. Ruberti, P. Decleva, and V. Averbukh, Phys. Chem. Chem. Phys. **20**, 8311 (2018).
[32]D. V. Shalashilin and M. S. Child, J. Chem. Phys. **128**, 054102 (2008).
[33]M. Ronto and D. V. Shalashilin, J. Phys. Chem. A **117**, 6948 (2013).
[34]D. V. Shalashilin, J. Chem. Phys. **130**, 244101 (2009).